Fe-zeolites as catalysts for chemical oxidation of MTBE in water with H_2O_2

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ABSTRACT

The heterogeneous catalytic wet oxidation of methyl tert-butyl ether (MTBE) with hydrogen peroxide, catalyzed by the iron-containing zeolites Fe-ZSM5 and Fe-Beta, was studied at ambient conditions and pH 7. The kinetics of MTBE degradation could be well-fitted to a pseudo-first-order model. Using Fe-ZSM5, the dependence of the reaction rate constant on hydrogen peroxide and catalyst concentration was determined. Furthermore, the formation and oxidation of tert-butyl alcohol and tert-butyl formate as intermediates of MTBE oxidation were studied. A comparison of the reaction rates of MTBE, trichloroethylene and diethyl ether in the Fe-ZSM5/H_2O_2 system revealed that adsorption plays a positive role for the degradation reaction.

Comparing the two types of Fe-containing zeolites applied in this study, Fe-Beta showed a lower catalytic activity for H_2O_2 decomposition and also MTBE degradation. However, in terms of utilization of H_2O_2 for MTBE degradation Fe-Beta is advantageous over Fe-ZSM5. This could be explained by the stronger adsorptive enrichment of MTBE on the Fe-Beta zeolite. This study shows that Fe-containing zeolites are promising catalysts for oxidative degradation of MTBE by H_2O_2.

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1. Introduction

Oxygenated compounds are added to gasoline in order to improve fuel combustion efficiency and to lower exhaust emissions of CO and hydrocarbons. Examples of these compounds are alcohols (as methanol, ethanol, isopropyl alcohol, isobutyl alcohol and tert-butyl alcohol) and ethers (as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME) and diisopropyl ether (DIPE)) [1,2]. MTBE is the most important fuel oxygenate used worldwide, and since 1998 in USA and 2002 in the European Union it has been included in monitoring programs of volatile organic compounds (VOC). It is considered as a unique contaminant owing to its ability to move readily throughout various environmental compartments and to its resistance to degradation [3]. Due to its physical and chemical properties, MTBE remains in groundwater for a long time. For this reason, the contamination of water supplies by MTBE is a problem of increasing concern.

The physico-chemical properties of the fuel oxygenates (high water solubility, low Henry's law constant and low octanol–water partition coefficient [4]) make their treatment with conventional water cleaning technologies difficult, including air stripping and adsorption on granular activated carbon (GAC) [5–7]. Sutherland et al. [5] examined the treatment of MTBE using air stripping, ultraviolet (UV)/H_2O_2 and O_3/H_2O_2 advanced oxidation and GAC adsorption in a pilot plant. The authors concluded that at high water flow rates, air stripping tended to be the most adequate treatment in terms of economy and efficiency. At lower rates, all the techniques were competitive and the process selection could be based on factors other than cost. Similar results were obtained by Baus et al. [7] who found that MTBE removal by means of aeration requires high air-to-water ratios and therefore high operating costs. Baus et al. [7] also studied advanced oxidation processes (AOPs) and adsorption alternatives. The O_3/H_2O_2 doses necessary for sufficient elimination of MTBE were found to be higher than those typically applied in the waterworks. Finally, they found that MTBE is only poorly adsorbed on GAC [7].

Nowadays, AOPs are becoming more and more important technologies for wastewater treatment, especially for hardly biodegradable contaminants [8–13]. The processes are based on generating reactive radicals, mainly hydroxyl radicals, which oxidize the target organic pollutant. These radicals are the second most powerful oxidants next to fluorine [14]. Ozone and hydrogen peroxide are the most often used substances to generate hydroxyl radicals, ultraviolet (UV) irradiation, catalysts or a combined application of O_3 and H_2O_2 are used to initiate the reaction. The high energy consumption for generating ozone by silent electrical

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discharges makes its use expensive. Additionally, its limited water solubility and its short lifetime make its application inconvenient. Hydrogen peroxide is a safer reactant than ozone. Catalytic activation of H_2O_2 is achieved, e.g. by the Fenton mechanism summarized below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \qquad (2)$$
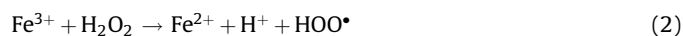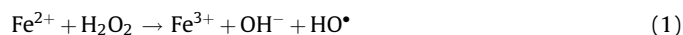
The classical Fenton reagent consists of a homogeneous solution of iron ions and hydrogen peroxide. It is a well-known and efficient oxidant for organic compounds dissolved in water [9,12,15–18]. The main drawbacks are that the use of metal salts as catalyst requires their subsequent removal from the treated water, mostly as iron oxide sludge, and the necessity of working at low pH (about pH 3) to achieve acceptable conversion rates. In recent years, increasing attention has been paid to research on heterogeneous Fenton-like systems as alternatives in order to overcome these problems. Either solid iron oxides [19] or iron species immobilized on solid supports such as zeolites [14,20–22], mesoporous solids [23] or Nafion membranes [24] have been applied. Zeolites offer various properties which can give them advantages over other supports: (i) as alumosilicate materials they are resistant to oxidation, (ii) iron can be easily introduced due to their ion-exchange capacity, and (iii) they possess unique sorption properties with respect to smaller organic molecules. Adsorption affinity and capacity with respect to a certain compound depend on the hydrophobicity of adsorbate and zeolite and the congruence of molecule and pore sizes. These sorption properties can be utilized in the case of Fe-zeolite catalysts for favored enrichment of the target organic contaminants in the vicinity of the catalytic centers. Non-target consumers of the reactive species can be discriminated due to their hydrophilicity (in the case of inorganic ions) or size (in the case of dissolved natural organic matter). Therefore, sorptive enrichment of the contaminant in the zeolite might lead to a higher rate and a more efficient utilization of the formed hydroxyl radicals in contaminant degradation.

Fe-containing zeolites have been intensively studied as catalysts for N_2O decomposition and selective catalytic reduction (SCR) of nitrogen oxides by NH_3 or hydrocarbons, i.e. for exhaust treatment [25–28]. Various preparation procedures have been proposed in order to introduce extra framework iron into zeolites including liquid and solid ion exchange or chemical vapour deposition which are usually followed by a calcination step [25,27,28]. In most cases, depending on preparation method and Fe content, various coexisting iron species are produced, ranging from isolated iron ions via dimers and small oligonuclear Fe_xO_y clusters

inside the pores up to Fe_2O_3 particles on the external surface [27,28].

Most of the studies conducted on wet peroxide oxidation using Fe-zeolite catalysts have been focused on phenolic compounds [20,21,29–31]. However, MTBE is known to be adsorbed with high affinity by various zeolites [32–34] and it has been shown to be degradable by AOPs such as treatment by Fenton's reagent [35,36] or UV/H_2O_2 and O_3/H_2O_2 [5,7]. Thus, as a continuation of a wider study related to theoretical and experimental analysis of water treatment techniques of fuel oxygenates, we here report about the catalytic activity of Fe-containing zeolites in the wet peroxide oxidation of MTBE at ambient conditions and pH 7. A working pH in the near neutral range is especially beneficial for the treatment of groundwater, which usually has a high natural buffer capacity. Acidification, as necessary for the homogeneous Fenton process, is rather uneconomic in this case.

Isotherms and kinetics of the adsorption of MTBE into the Fe-zeolites were also studied. The kinetics of the MTBE degradation was analyzed using various concentrations of hydrogen peroxide and catalyst. The formation and oxidation of tert-butyl alcohol (TBA) and tert-butyl formate (TBF), the most problematic degradation intermediates of MTBE with respect to potential toxicity, were studied. Several experiments with other organic compounds were carried out in order to study the influence of adsorption in the oxidation process. Finally, the catalyst was used after washing procedures to study the relevance of leaching in the process.

2. Experimental

2.1. Materials and methods

All the chemicals and organic solvents were obtained with a purity of higher than 99% from Merck (Germany). The humic acid was purchased from Carl Roth GmbH, Karlsruhe, Germany and was used without further purification. The applied zeolites Fe-ZSM5 and Fe-Beta were provided by Süd-Chemie Zeolites (Bitterfeld, Germany).

Preliminary experiments showed that the original Fe-Beta catalyst contains a relatively large fraction of labile iron which would be leached during application in water. Therefore, this catalyst was washed prior to its use in reaction experiments in order to obtain a stable product: three sequential washing steps were conducted whereby 2 g of catalyst was suspended in 40 mL of 0.1 M KNO_3 solution adjusted to pH 3 with HNO_3 and shaken for at least 2 h. The catalyst was then washed twice with deionized water and dried at 50 °C. According to the results of X-ray fluorescence

Table 1
Characteristic properties of the applied organic compounds and zeolites: octanol–water partition coefficient (K_{OW}), water solubility (S_w), rate constant for the reaction with hydroxyl radical (k_n), kinetic diameter, pore sizes, iron content and SiO_2/Al_2O_3 molar ratio determined by XRF, and Freundlich constants for the adsorption isotherms of MTBE on both catalysts.

Compound	log K_{OW}[a]	S_w (g L^{-1})[a]		k_n (10^8 L mol^{-1} s^{-1})[b]	Kinetic diameter (Å)[c]
MTBE	0.94	44.3[d]		16	6.2
TCE	2.42	1.47		29–43	5.6
Diethyl ether	0.89	60.4		29–42	5.2[e]
Zeolite	Iron content (wt%)	Maximum free pore diameter (Å)[e]	SiO_2/Al_2O_3	K (mg/kg)(L/mg)$^{1/n}$	$1/n$
Fe-ZSM5	2.2	5.6	26	18.2	1.26
Fe-Beta	1.3	7.5	42	8414	0.57

[a] [47].
[b] [49].
[c] [50].
[d] [48].
[e] [40].

analysis[1] the iron content of the Fe-Beta catalyst treated in this way was 0.97 wt% compared to 1.29 wt% before washing. The Fe-ZSM5 had a slightly higher Fe content of 2.2 wt%. This catalyst had already showed a good stability of the iron content and catalytic activity during washing with tap water (see Section 3.7). Therefore, it was used without a preliminary washing step. The main properties of the chemicals used in the study and the zeolites are summarized in Table 1.

H_2O_2 content was determined by photometric measurements using a solution of titanyl sulfate and a UV mini 1240 Shimadzu spectrophotometer [37]. The concentrations of the organic compounds in the reaction solutions were determined by GC–MS analysis (GC HP 5890 and MS HP 5972 mass spectrometer detector, Agilent, Germany) operating in the selected ion monitoring mode and with a JW DB-624 capillary column (film thickness: 1.8 μm). For MTBE, trichloroethylene (TCE), diethyl ether, TBA and TBF a headspace analysis method using gas-tight microliter syringes (100 μL) was applied. GC analyses of the headspace samples were carried out isothermally at 373 K when only MTBE degradation was monitored or at 333 K when MTBE together with its products TBA and TBF were analyzed.

The monitoring of the reaction was carried out via solvent extraction of aliquots of the reaction suspension in those cases where significant adsorption of the organic compounds to the zeolites was observed (see below). In the analysis of the extracts a temperature ramp (5 K min^{-1}, from 338 to 353 K (latter held for 2 min)) was used. The relative standard deviation of the headspace analysis method was in the range of σ = 7% and that for GC–MS analysis of the solvent extracts was in the range of σ = 6%.

For determination of the total organic carbon (TOC) content, a carbon detector was applied which consisted of a two-zone combustion unit (700 °C combustion zone, 800 °C catalytic post-oxidation zone with 0.5 wt% Pt/Al_2O_3 as catalyst), membrane dryer (PermaPure, USA) for drying of the combustion gas and NDIR detector (type 34364, Saxon Junkalor, Germany) for CO_2 detection. Potassium hydrogen phthalate was used for calibration. In order to remove inorganic carbon prior to analysis, samples were acidified (pH ≤ 5) and purged with N_2 for 5 min. Due to the fact that the purging can result in a loss of volatile organic compounds, the obtained TOC value has to be considered as a lower limit.

2.2. Sorption kinetics and isotherms

In order to determine the kinetics of the sorption process, 200 mL of a suspension of the zeolite in neutral deionized water with a concentration of 5 or 15 g L^{-1} for Fe-Beta and Fe-ZSM5, respectively, was filled into a 250 mL-flask with Mininert® valve and shaken overnight on a horizontal shaker. The sorption experiment was then started by adding an aqueous stock solution of MTBE resulting in a total concentration of C_{MTBE} = 100 mg L^{-1} in the suspension. The flasks were placed on a horizontal shaker. At several points in time the concentration of the freely dissolved fraction of MTBE was determined by headspace analysis.

Furthermore, the desorption kinetics of the process was studied. Samples of the adsorption experiment described above were allowed to equilibrate over a time period of 4 days, after which the samples were centrifuged and the clear water phase decanted. The zeolite was transferred into a 250 mL-flask with a Mininert® valve; the desorption process was then started by addition of 200 mL of neutral deionized water and the flasks were shaken on a horizontal shaker. After various time periods, the concentration of the freely dissolved fraction of MTBE was determined by headspace analysis.

The determination of equilibrium sorption isotherms was carried out at room temperature (25 ± 2 °C). They were obtained by preparing several suspension samples with different concentrations of zeolite and different total concentrations of MTBE in 250 mL-flasks with Mininert® valves. After 24 h of shaking on a horizontal shaker, the concentration of the freely dissolved fraction was determined by headspace analysis.

2.3. Heterogeneous Fenton reaction

A stock solution of 1 g L^{-1} of MTBE in deionized water was used to prepare samples with a concentration of 100 mg L^{-1}. The samples were filled into 120 mL-flasks with a Mininert® valve for headspace sampling and two additional valves which could be used to depressurize the reactor and to add reagent solutions. The catalyst was then added to the reactor. The pH was adjusted to 7 and readjusted during the reaction if necessary by adding dilute NaOH. Adsorption was allowed to come to equilibrium for at least 24 h, while the samples were shaken on a horizontal shaker. Afterwards, the concentration of the freely dissolved fraction of the organic compounds was determined by headspace analysis. The reaction was started by adding a defined amount of H_2O_2 solution (30 wt%). The concentration of H_2O_2 was monitored by photometry as explained above. In order to keep the concentration of H_2O_2 approximately constant (±20% of the starting value), further H_2O_2 was either periodically added into the reactor manually or fed continuously using a syringe pump (Lambda vit-fit). The latter option was chosen in the experiments with a high concentration of Fe-ZSM5 (≥25 g L^{-1}) where the decomposition of H_2O_2 was fast (half-life ≤ 10 min). The flasks were vigorously shaken on a horizontal shaker.

In cases of low sorption of the organic compounds to the zeolites (sorbed fraction ≤ 15%) the residual concentrations of the organic compounds were determined by headspace analysis in the course of the reaction. Otherwise, headspace analysis was only applied to determine the concentration of the freely dissolved fraction whereas the total remaining concentration of the organic compounds was obtained by liquid–liquid extraction. In this case, 0.5 mL-aliquots were retained, spiked with 0.22 mmol of sodium thiosulfate in order to stop the reaction (complete consumption of H_2O_2) and extracted with 0.5 mL of n-hexane or dichloromethane, containing toluene as an internal standard, by shaking for at least 2 h. While in the case of ZSM5-containing suspensions sufficient recoveries (≥90%) of all analytes were achieved with both solvents, dichloromethane was more efficient for extraction of MTBE from suspensions of Beta zeolite (recovery ≥ 90%). The extracts were analyzed by GC–MS as described above. The kinetics of the degradation reaction was characterized by the change in the residual fraction of MTBE (C/C_0) over time, whereby C/C_0 refers to the total amount of MTBE present in the reaction suspension. Losses due to volatilization during the reaction were insignificant for MTBE and all other model compounds.

In order to carry out the competition reaction experiments with diethyl ether and TCE, aqueous stock solutions with 1 g L^{-1} of the respective compound were prepared. These stock solutions were used to prepare the samples containing two organic compounds, each at a concentration of 100 mg L^{-1}. For the experiment with humic acid, a stock solution of 1 g L^{-1} was prepared. In order to dissolve the humic acid, a solution of NaOH was used (50 mL of 0.02 M NaOH for 100 mg humic acid). Finally, the pH of the humic acid solution was adjusted with dilute HCl to pH 7.

3. Results and discussion

3.1. Decomposition of H_2O_2 by the Fe-zeolites

As Fig. 1 shows, the decomposition of H_2O_2 on Fe-ZSM5 and Fe-Beta follows a pseudo-first-order kinetics. The catalyst activity

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[1] Detailed information about analysis conditions available as Supplementary material.
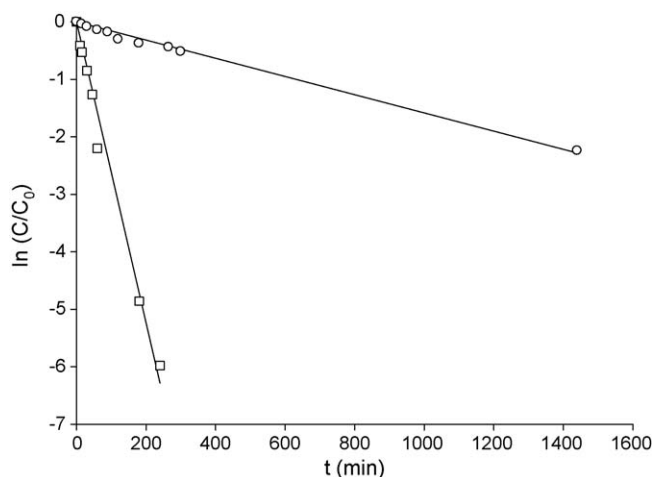
Fig. 1. Decomposition of H_2O_2 ($C_{0,H_2O_2} = 7.5\,g\,L^{-1}$) in catalyst suspension of Fe-ZSM5 ($C_{cat} = 5\,g\,L^{-1}$) ($\square$) and Fe-Beta ($C_{cat} = 50\,g\,L^{-1}$) ($\bigcirc$).

(A) calculated with Eq. (3)

$$A = \frac{k_1}{C_{cat}} \tag{3}$$

from the pseudo-first-order rate constant (k_1) of the reaction and the catalyst concentration (C_{cat}) is $3.7 \times 10^{-3}\,L\,g^{-1}\,min^{-1}$ for H_2O_2 decomposition on Fe-ZSM5. For Fe-Beta it is lower by about two orders of magnitude ($3.0 \times 10^{-5}\,L\,g^{-1}\,min^{-1}$). The prevailing assumption in the literature is that H_2O_2 is decomposed at the iron sites on the zeolite by a Fenton type mechanism whereby hydroxyl radicals are formed [21,29,30,37]. These radicals are available to oxidize organic compounds dissolved in water or adsorbed on/within the zeolite. The difference in the catalytic activity for H_2O_2 decomposition between the two Fe-containing zeolites probably cannot be simply explained by the difference in the total Fe content which is only a factor of about two (Table 1). In fact, the speciation of the iron has to be considered as an important factor as well. Structure–activity correlations based on a wider range of Fe-zeolite samples will be needed in order to elucidate the role of the various possible iron species in the catalytic process.

### 3.2. Isotherms and kinetics of MTBE adsorption by the Fe-zeolites

The adsorption isotherm of MTBE on Fe-ZSM5 corresponds to a type V in the BDDT [39] system, whereas for MTBE on Fe-Beta a type I isotherm is observed. A type V isotherm indicates that once a molecule has become adsorbed at a primary adsorption site, the adsorbate–adsorbate interactions significantly increase the driving force of the further adsorption process [39]. Nevertheless, within the concentration range studied, the isotherms of MTBE adsorption on Fe-ZSM5 and Fe-Beta can be reasonably well described by the Freundlich model:

$$q_e = KC_{eq}^{1/n} \tag{4}$$

where q_e is the equilibrium concentration of the adsorbate in the solid phase ($mg\,kg^{-1}$) and is obtained by the following equation:

$$q_e = \frac{(C_0 - C_{eq})V}{m} \tag{5}$$

C_{eq} is the equilibrium aqueous phase concentration ($mg\,L^{-1}$) and C_0 is the initial aqueous phase concentration ($mg\,L^{-1}$) of the adsorbate, V is the volume (L) of adsorbate solution, m is the mass of zeolite (kg) and K and $1/n$ are the Freundlich constants. The
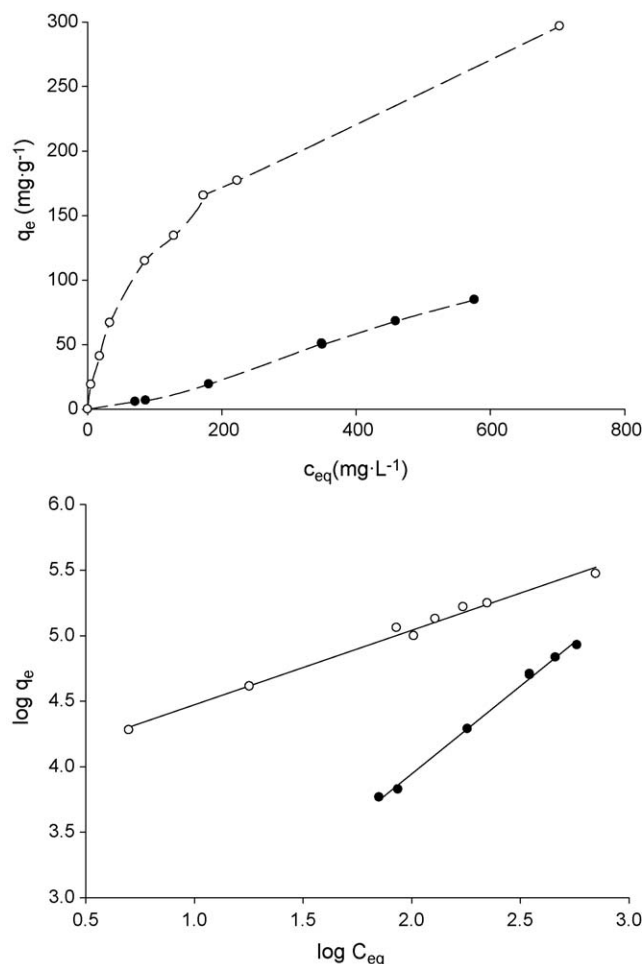
**Fig. 2.** Adsorption isotherms for MTBE adsorbed on Fe-ZSM5 ($\bullet$) and Fe-Beta ($\bigcirc$) with Freundlich model fit.

linearized form of the Freundlich equation for regression is:

$$\log q_e = \log K + \frac{1}{n} \log C_{eq} \tag{6}$$

Fig. 2 shows the isotherms for MTBE sorption in both zeolites at ambient conditions. The respective Freundlich parameters are given in Table 1. Isotherms for MTBE showed that the sorption affinity was higher for Fe-Beta than for Fe-ZSM5. According to the higher SiO_2/Al_2O_3 ratio (Table 1) the Fe-Beta zeolite can be considered as slightly more hydrophobic than the Fe-ZSM5. However, the two zeolites also differ markedly in their pore size: while ZSM5 has a 10-ring channel structure (minor and major axis dimensions of 5.1 Å × 5.5 Å and 5.4 Å × 5.6 Å for the sinusoidal and straight channels, respectively), the 12-ring channel system of Beta zeolite has larger pore dimensions (6.5 Å × 5.6 Å and 7.5 Å × 5.7 Å) [40]. Based on its kinetic diameter (6.2 Å) the MTBE molecule should be able to enter the pores of the Beta zeolite, while the compatibility with the pore opening is not self-evident in case of the ZSM5 zeolite. However, a considerable amount of up to 1 mmol g^{-1} MTBE was adsorbed by Fe-ZSM5 in our experiments (Fig. 2), which corresponds to a loading of about 0.2 mmol m^{-2} of external zeolite surface.[2] This amount is by one order of magnitude higher than the value expected for a monolayer based on the dimensions of the MTBE molecule. This clearly shows that the

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[2] In order to estimate the external surface of the zeolite particles their diameter was assumed to be 1 μm. This is the lower limit of the particle size range specified by the supplier (1 - 10 μm) and confirmed by microscopy.
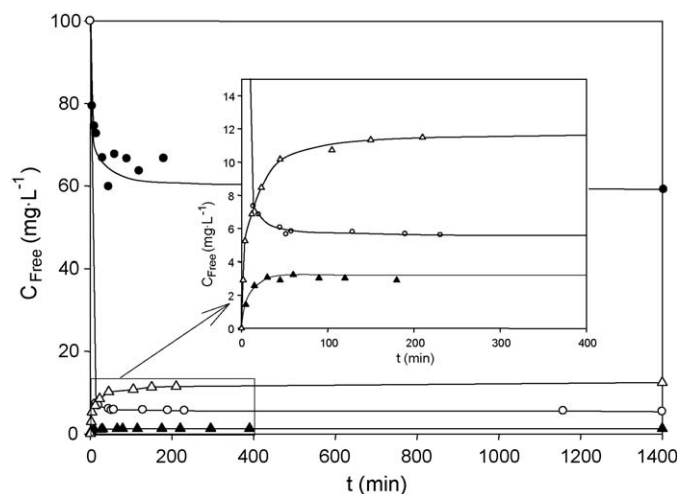
Fig. 3. Course of the concentration of MTBE in the aqueous phase (C_{Free}) in the adsorption (○) and desorption (△) experiments with MTBE on Fe-ZSM5 (filled symbols) and Fe-Beta (open symbols).

adsorption of MTBE on Fe-ZSM5 occurs within the zeolite cavities. Based on a similar evaluation of the adsorption capacity Centi et al. [41] came to the same conclusion for adsorption of MTBE to a ZSM5 zeolite. Furthermore, Centi et al. observed a higher degree of MTBE adsorption on a Beta zeolite than on a ZSM5 zeolite exhibiting the same SiO_2/Al_2O_3 ratio (and therefore similar hydrophobicity). From this result one can conclude that the larger pore dimension of Beta zeolite is more favorable for the hosting of the MTBE molecule. By means of Monte Carlo and molecular dynamics simulations of the adsorption of MTBE into various zeolites, Yazaydin and Thompson [42] predicted a higher adsorption capacity for all-silica Beta zeolite compared to silicalite, despite the fact that both zeolites have similar total pore volumes. Silicalite is very similar to ZSM5 since both have the same MFI type framework with the only difference that silicalite is purely siliceous. Based on the results of the simulations, the authors concluded that MTBE molecules are only adsorbed in the intersections of the straight and zigzag pores of MFI type zeolites, while in Beta zeolite all pores are large enough to accommodate MTBE molecules [42].

In order to make possible a comparison of the timescale of reaction with that of sorption and desorption of MTBE on both zeolites, a simple sorption–desorption experiment was performed (Fig. 3). The sorption process of MTBE on both zeolites closely approached equilibrium within 30 min. No significant changes were observed between measurements after 1 and 24 h. The sorbed fractions of MTBE with Fe-ZSM5 (15 g L^{-1}) and Fe-Beta (5 g L^{-1}) were about 30 and 90%, respectively. The desorption step of the experiment was started by removing the aqueous phase with the remaining freely dissolved fraction of MTBE and adding fresh water. Re-equilibration was almost complete within 30 min in the case of Fe-ZSM5 and within 2 h for Fe-Beta. However, also in the latter case about 80% of the equilibrium level is achieved within the first 30 min after adding fresh water.

These experiments provide clear evidence that the sorption–desorption processes are fast compared to the timescale of the chemical reaction, as will be shown later in the text. Thus, sorption–desorption processes can be considered to be close to equilibrium during the course of the reaction.

3.3. Heterogeneous catalytic wet oxidation with Fe-ZSM5/H$_2$O$_2$

The observed kinetics of degradation of the organic compounds in the Fe-ZSM5/H$_2$O$_2$ system was reasonably well fitted to a
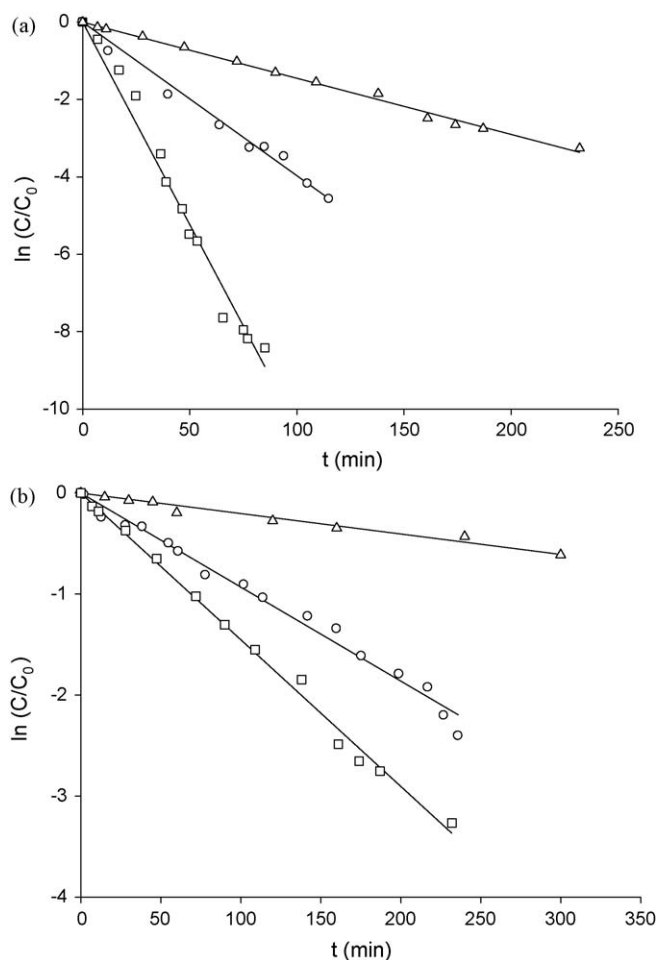
Fig. 4. Reaction of MTBE in an aqueous suspension of Fe-ZSM5. (a) Influence of the hydrogen peroxide concentration ($C_{0,MTBE}$ = 100 mg L^{-1}, C_{cat} = 25 g L^{-1}, $C_{H_2O_2}$ = 1.0 g L^{-1} (△); 1.9 (○); 6.3 (□) g L^{-1}). (b) Influence of the catalyst concentration ($C_{0,MTBE}$ = 100 mg L^{-1}, $C_{H_2O_2}$ = 1.0 g L^{-1}, C_{cat} = 5 g L^{-1} (△); 15 g L^{-1} (○); 25 g L^{-1} (□)).

pseudo-first-order model which can be formulated as

$$\ln C - \ln C_0 = -k_1 t \tag{7}$$

where C is the concentration of the compound at any time (t), C_0 is the initial concentration and k_1 is the pseudo-first-order rate constant. When the catalyst was removed from the reaction solution by means of centrifugation, no significant degradation of MTBE in the supernatant was observed. That means the reaction indeed takes place at the catalyst. Furthermore, no degradation of MTBE by the catalyst is observed in the absence of H$_2$O$_2$.

The effects of the H$_2$O$_2$ and catalyst concentrations on the degradation of MTBE in the presence of Fe-ZSM5 were analyzed, showing that an increase in these parameters increases the pseudo-first-order reaction rate constant (Fig. 4, Table 2).

Table 2
Rate constants (confidence interval, P = 0.95) and correlation coefficients for the first order kinetic model at various catalyst (C_{cat}) and hydrogen peroxide ($C_{H_2O_2}$) concentrations.

C_{cat} (g L^{-1})	$C_{H_2O_2}$ (g L^{-1})	k_1 (10^{-3} min^{-1})	R
5	1.0	3.3 ± 0.2	0.974
15	1.0	9.3 ± 0.3	0.987
25	1.0	14.5 ± 0.4	0.993
25	1.9	40 ± 2	0.986
25	6.3	105 ± 4	0.982
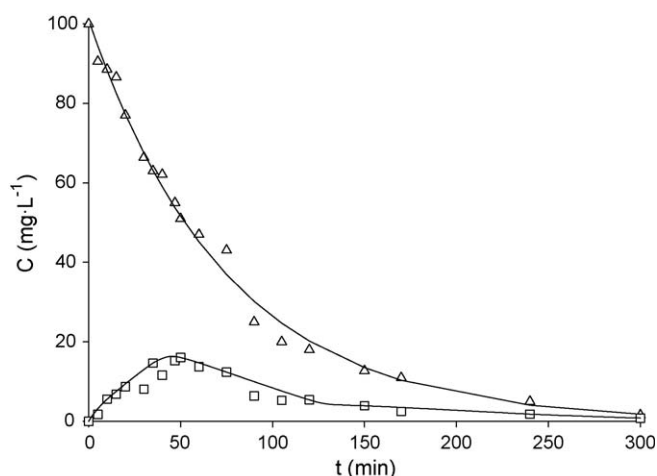
Fig. 5. Evolution of the MTBE ($\triangle$) and tert-butyl formate ($\square$) concentration during the reaction in an aqueous suspension of Fe-ZSM5 ($C_{cat} = 5$ g L^{-1}, $C_{0,MTBE} = 100$ mg L^{-1}, $C_{H_2O_2} = 7.5$ g L^{-1}).

The conversion of MTBE in the experiments with a catalyst concentration of 25 g L^{-1} and a concentration of hydrogen peroxide of 1 g L^{-1} was 96% after 4 h, achieving a conversion higher than 99% when the concentration of hydrogen peroxide was increased up to 7 g L^{-1}. The evolution of the kinetic rate constant with the hydrogen peroxide concentration has a nearly linear trend in the concentration range studied (Figure S1 in Supplementary material). Since with increasing concentration H$_2$O$_2$ itself can become a relevant consumer of hydroxyl radicals, the observed trend cannot be arbitrarily extrapolated; rather, the existence of an optimum H$_2$O$_2$ concentration is to be expected.

The influence of the catalyst concentration on the rate of MTBE degradation was also analyzed, keeping the concentration of hydrogen peroxide at 1 g L^{-1}. With a low load of catalyst (5 g L^{-1}) the MTBE conversion achieved within 5 h was 50%. However, with 25 g L^{-1} of catalyst conversion achieved was 96% in less than 3 h. The correlation between the pseudo-first-order rate constant of MTBE degradation and the catalyst concentration also has a nearly linear trend in the concentration range studied (Figure S2 in Supplementary Material). The catalytic activity with respect to MTBE degradation was 5.8×10^{-4} L g^{-1} min^{-1}.

3.4. Tert-butyl alcohol and tert-butyl formate as intermediates of MTBE oxidation with Fe-ZSM5/H$_2$O$_2$

The pathways of MTBE degradation by hydroxyl radicals have been intensively studied over the last decade [35,43,44]. TBA, TBF, methyl acetate and acetone have been identified as main intermediates in the Fenton and photo-Fenton oxidation of MTBE [35,44]. Intermediates found in smaller amounts include alcohols <C$_4$, carboxylic acids and formaldehyde. [35]. A detailed analysis of intermediates formed in the heterogeneous process with Fe-zeolites would have been outside the scope of this work. However, as a first step, intermediates having a tert-butyl group in their structure, i.e. TBA and TBF were monitored, due to the concerns related to their potential toxicity. Fig. 5 shows the results of an experiment whereby 100 mg L^{-1} of MTBE were degraded in the presence of 5 g L^{-1} Fe-ZSM5 and 7.5 g L^{-1} H$_2$O$_2$. After a reaction time of 4 h a residual TOC of 29 mg L^{-1} was measured which corresponds to 36% of the initial carbon concentration caused by MTBE. At the same time the concentration of MTBE had been reduced by 95%. TBA and TBF showed the typical concentration profile of an intermediate for which formation and further degradation occur simultaneously. TBA (data not shown) was found only in trace amounts close to the detection limit of the headspace method (≤ 2 mg L^{-1}). TBF reached a maximum concentration equal to about 18% of the initial molar concentration of MTBE. However, its degradation proceeds in the same timescale as the degradation of MTBE (Fig. 5). These results indicate that even though TBA and TBF can be formed in the heterogeneous oxidation of MTBE they will not persist but can be further degraded.

3.5. Competition experiments with Fe-ZSM5 as catalyst

Competition experiments were carried out with the intention of comparing the reactivity of various compounds having different properties with respect to molecular size and chemical reactivity. In each case, two compounds (initial concentration 100 mg L^{-1} of each) were applied simultaneously in the same reaction system in order to assure identical reaction conditions. Differences in the reaction rates of the various compounds can be due to different intrinsic reactivities towards the reactive species. On the other hand, they can also be caused by qualitative or quantitative differences in the adsorption to the zeolites which result in different local contaminant concentrations in the vicinity of the sites where the reactive species are formed.

The compounds involved in this study were (i) TCE, as a model compound with a C–C double bond, (ii) diethyl ether, because of its chemical similarity to MTBE but smaller size, and (iii) a humic acid, because humic acids are ubiquitous natural compounds present in groundwaters.

The experiment with diethyl ether was carried out in order to see how the size of the molecule can affect the degradation rate of the aliphatic ethers at the Fe-ZSM5 catalyst. At a catalyst concentration of 5 g L^{-1} the adsorbed fraction of diethyl ether is 87% while for MTBE it is only 15% (Table 3). Since the two ethers are very similar in their hydrophobicities, the more favorable adsorption of diethyl ether is probably due to a better fit between molecule and zeolite pore size (Table 1). The rate constant for hydroxyl radical attack in aqueous solution is 1.8–2.6 times higher for diethyl ether than for MTBE (Table 1). However, the difference in the degradation rates of the two compounds in the Fe-ZSM5/H$_2$O$_2$ system is much more pronounced. The observed rate constant for degradation of diethyl ether is 7 times higher compared to MTBE. The observed preference of diethyl ether, which is extensively adsorbed by the Fe-ZSM5 zeolite, points to a positive effect of adsorptive enrichment in the zeolite pore system on the degradation rate.

Diethyl ether and TCE have very similar rate constants for reaction with hydroxyl radicals. Adding diethyl ether and TCE simultaneously to the Fe-ZSM5 suspension resulted in nearly the same degree of sorption for the two compounds ($F_{ad} = 0.6$), as shown in Table 3. However, TCE reacted much faster after addition of H$_2$O$_2$. Its pseudo-first order rate constant is about 20 times higher than that of diethyl ether. The different reactivities of diethyl ether and TCE can be due to several reasons. Firstly, the rate
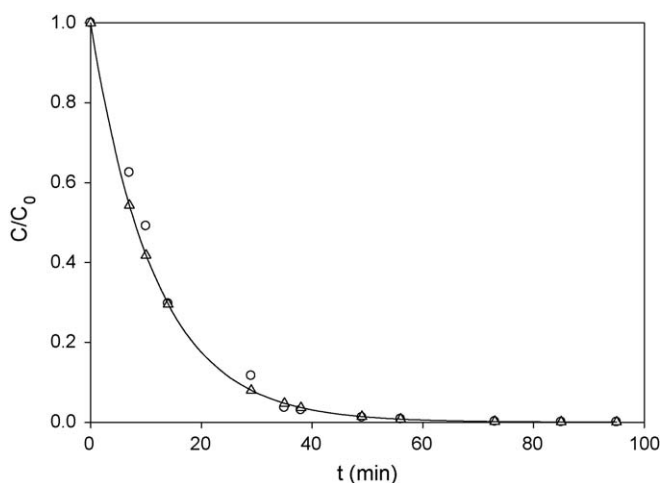
Table 3
Parameters of the competition reactions between MTBE, TCE and DEE. Adsorbed fraction (F_{ad}), pseudo-first rate constant (k_1) and ratio of the rate constants ($R_{(2/1)} = k_{1(2)}/k_{1(1)}$).

| Compound 1	Compound 2	$F_{ad(1)}$ (%)	$F_{ad(2)}$ (%)	$k_{1(1)}$ (min^{-1})	$k_{1(2)}$ (min^{-1})	$R_{(2/1)}$
MTBE	TCE	11	65	0.0080	0.40	50
MTBE	DEE	15	87	0.011	0.073	6.6
DEE	TCE	65	63	0.016	0.34	21

constants determined for homogeneous reaction of organic compounds with hydroxyl radicals in the solution phase might be not valid for reactions in the adsorbed state, e.g. due to another type of transition state for the reaction. However, we favour the hypothesis that the oxidation of the organic compounds involves reactive species which react with a selectivity different to that of hydroxyl radicals. As a saturated compound, diethyl ether can only be attacked by H-abstraction, whereas TCE is susceptible for addition of various less reactive radicals as well. Despite the fact that most authors adopt the hypothesis that hydroxyl radicals are formed from H_2O_2 in iron/zeolite systems [21,29,30,38] it has not yet been directly proven.

The comparison between MTBE and TCE degradation by Fe-ZSM5/H_2O_2 again shows a faster reaction for TCE, which is probably caused by the combined effect of better adsorption and higher intrinsic reactivity of TCE in this system.

Finally, the effect of the presence of humic acid on the degradation of MTBE in the Fe-ZSM5/H_2O_2 system was studied. Humic substances are ubiquitous constituents of natural surface water and groundwater, where they represent an important part of the dissolved organic carbon (DOC). The highest concentrations of humic substances are found in brown waters of, e.g. bogs where DOC concentrations of up to 30 mg L^{-1} are found [45], although the concentration of humic substances in groundwaters is usually below 10 mg L^{-1} [46]. Fig. 6 shows the results of MTBE degradation in the presence of a relatively high humic acid concentration of 100 mg L^{-1}. In this experiment the reaction was started after a pre-equilibration period of 24 h, i.e. within this period the catalyst was in contact with the aqueous solution containing MTBE and humic acid. At the beginning of the reaction $\geq$85% of MTBE were in the aqueous phase. That means, MTBE had to be continuously transported from the aqueous phase into the zeolite pores in order to be degraded. As shown in Fig. 6, the performance of the catalyst is not significantly affected in the presence of the humic acid. The fact that the humic acid macromolecules are excluded from entering into the zeolite pore space, largely eliminates their role as consumers of reactive species. Furthermore, even though the humic acid molecules can be adsorbed to the external surface of the zeolite particles, the access of the TCE molecules to the reactive sites is obviously not hindered. These findings open up the prospect that the catalyst may be suitable for the treatment of contaminated natural waters with moderate or even high humic acid contents.
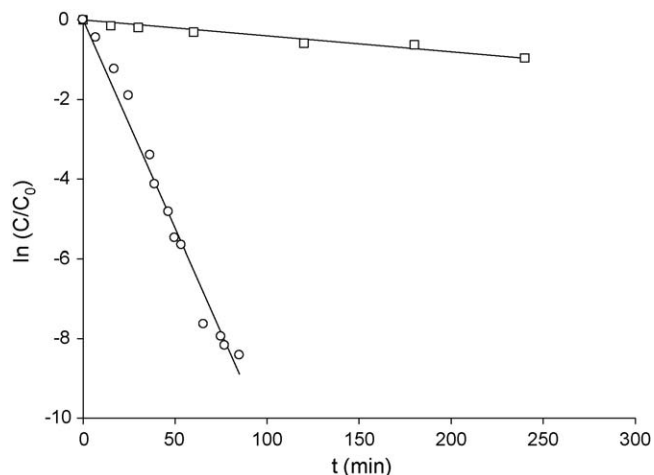
Fig. 7. Oxidation of MTBE (C_{cat} = 25 g L^{-1}, $C_{0,MTBE}$ = 100 mg L^{-1}, $C_{H_2O_2}$ = 6 g L^{-1}) using Fe-ZSM5 (○) and Fe-Beta (□).

3.6. Investigations with Fe-Beta zeolite exhibiting larger pore size

In order to see how the zeolite pore size affects the adsorption of MTBE and consequently the performance of the chemical oxidation, the iron-containing Fe-Beta zeolite with larger pore size was used. While MTBE appears to be slightly too large to neatly fit into the 10-ring pores of ZSM5, the fitting into the 12-ring pores of the Beta zeolite is expected to be much more favorable (see Table 1). As shown in Fig. 2, Fe-Beta has a much higher adsorption affinity for MTBE than Fe-ZSM5 has. In experiments with 100 mg L^{-1} of MTBE and 5 g L^{-1} of catalyst, an adsorption degree of 10% was found for Fe-ZSM5, whereas for Fe-Beta it was 90%.

Fig. 7 shows the results of batch experiments where the two catalysts were applied under identical conditions. The catalytic activity for MTBE degradation at the applied concentration of H_2O_2 (6 g L^{-1}) is 4.2×10^{-3} L g^{-1} min^{-1} for Fe-ZSM5 and 1.6×10^{-4} L g^{-1} min^{-1} for Fe-Beta.

As stated in Section 3.1, the catalytic activity for H_2O_2 decomposition is two orders of magnitude lower for the Fe-Beta catalyst compared to Fe-ZSM5. However, the activity for MTBE degradation is lower only by a factor of 20. It is reasonable to assume that a lower activity in H_2O_2 decomposition leads to a proportionally lower steady-state concentration of hydroxyl radicals (or any other reactive species formed from H_2O_2). Therefore, the MTBE degradation rate should be lower with Fe-Beta than with Fe-ZSM5. This was indeed observed; however, the decrease in the degradation rate of MTBE is lower than expected.

In order to compare the efficiency of H_2O_2 utilization for contaminant degradation in the two catalyst systems, the ratio of the moles of H_2O_2 consumed per mol of MTBE degraded was calculated for the initial reaction period, i.e. until the 100 mg L^{-1} initial concentration of MTBE in the catalyst suspension was reduced by 50%. This ratio (moles H_2O_2/mol MTBE) was 310 for Fe-ZSM5 and 47 for Fe-Beta as catalyst (at C_{cat} = 25 g L^{-1}, $C_{H_2O_2}$ = 6 g L^{-1}, $C_{0,MTBE}$ = 100 mg L^{-1}). Consequently, comparing the two catalysts, H_2O_2 is more efficiently utilized for MTBE degradation in the case of Fe-Beta. This is plausible, taking into account the better adsorption of MTBE by this zeolite. The enrichment of MTBE in proximity to the catalytically active sites will increase the probability of a reaction between the transient reactive species and MTBE molecules.

3.7. Effect of washing the catalyst

Leaching of iron is a critical parameter for the stability of the catalyst under environmental conditions. In order to see how the

Fig. 6. Oxidation of MTBE in the absence (△) and presence (○) of humic acid in an aqueous suspension of Fe-ZSM5 (C_{cat} = 25 g L^{-1}, $C_{0,MTBE}$ = 100 mg L^{-1}, $C_{0,HA}$ = 100 mg L^{-1}, $C_{H_2O_2}$ = 4 g L^{-1}). Reaction was started by adding H_2O_2 after a pre-equilibration period of 24 h.

possible leaching of iron and the use of tap water can affect the catalytic activity of the Fe-zeolites, for each catalyst parallel experiments were conducted: (I) in deionized water, (II) in tap water and (III) in tap water after 4 washing steps (5 g catalyst suspended in 100 mL of tap water, shaken for 1 h, than centrifugation).

In the series of experiments with Fe-ZSM5, the catalyst concentration was $5 \, g \, L^{-1}$, the hydrogen peroxide concentration was maintained at $4.5 \, g \, L^{-1}$ and the initial MTBE concentration was $100 \, mg \, L^{-1}$. The pseudo-first-order rate constant for MTBE degradation in case (I) was $(0.51 \pm 0.04) \, h^{-1}$ while for the cases (II and III) it was $(0.23 \pm 0.01) \, h^{-1}$ and $(0.22 \pm 0.01) \, h^{-1}$, respectively.

In the series with Fe-Beta, the conditions were $C_{cat} = 50 \, g \, L^{-1}$, $C_{H_2O_2} = 6 \, g \, L^{-1}$ and $C_{0,MTBE} = 100 \, mg \, L^{-1}$. With this catalyst the MTBE reaction rate constant for case (I) was $(0.55 \pm 0.03) \, h^{-1}$ while for the cases (II and III) it was $(0.43 \pm 0.01) \, h^{-1}$ and $(0.45 \pm 0.04) \, h^{-1}$, respectively.

These results show that MTBE degradation in tap water is slightly slower than in deionized water under otherwise identical conditions. This means that the inorganic components of tap water (e.g. bicarbonate) do not out-compete the organic pollutant MTBE. The washing steps did not significantly change the catalytic activity of the two Fe-zeolites for MTBE degradation in tap water. That means that the catalytically active iron species of the studied Fe-zeolites are fairly stable against leaching by tap water. In future studies their long-term stability will be tested in column experiments.

3.8. Comparison of the catalysts

In principle both materials under study, Fe-ZSM5 and Fe-Beta, are applicable as catalysts for the oxidation of MTBE in water with H_2O_2. Fe-ZSM5 has a higher catalytic activity for H_2O_2 decomposition and MTBE degradation. However, Fe-Beta has a considerably higher adsorption capacity for MTBE due to a more favorable fit of molecule and zeolite pore size.

For the technical realization of an oxidation process using Fe-zeolites as catalyst, adsorption and reaction can be combined in (I) a continuous or (II) an intermittent operation mode (see also Table S1 in Supplementary material). In mode (I), H_2O_2 is continuously fed to the contaminated water stream which enters the reactor. In mode (II), MTBE is removed from the contaminated water primarily by means of adsorption on the Fe-zeolite combined with intermittent regeneration of the spent adsorbent by flushing with H_2O_2 solution.

Comparing the two catalysts, the better adsorption of MTBE in the case of Fe-Beta might compensate the disadvantage of its lower catalytic activity in both modes of operation. In mode (I), the lower catalytic activity would call for longer residence times in the reactor in order to achieve a given extent of contaminant removal. However, at the same reactor size, longer residence times are indeed already achieved with Fe-Beta than with Fe-ZSM5 due to the fact that there is a much stronger adsorptive retardation of MTBE. In case (II), lower catalytic activity increases the duration of the adsorbent regeneration stage. However, the higher adsorption capacity of Fe-Beta allows a higher throughput of contaminated water until regeneration becomes necessary. Furthermore, the more efficient utilization of H_2O_2 for MTBE degradation in the case of Fe-Beta is certainly advantageous for the reduction of the operating costs.

Detailed column studies with the two types of catalysts will have to be conducted in order to elucidate which of them is the most suitable for oxidative treatment of MTBE-contaminated water.

4. Conclusions

Adsorption isotherms of MTBE on Fe-ZSM5 and Fe-Beta were studied, showing that Fe-Beta has a higher adsorption capacity for this compound. The adsorption/desorption kinetics were found to be similar for the two catalysts. Under identical reaction conditions, Fe-ZSM5 showed a higher catalytic activity for H_2O_2 decomposition and MTBE degradation. However, the utilization of H_2O_2 for MTBE degradation was more efficient in the case of Fe-Beta.

Attention was paid to the formation of TBA and TBF, being possible dangerous intermediate products of MTBE oxidation. While TBA was formed only in trace amounts, TBF represents a significant intermediate which, however, is subject to fast further degradation.

Results of competition experiments using Fe-ZSM5 and compounds with different adsorption tendencies on this zeolite point to the positive effect of adsorption in the reaction. This is plausible since adsorption leads to enrichment of the contaminant in the vicinity of the reactive sites. The presence of a high concentration of humic acid $(100 \, mg \, L^{-1})$ did not negatively affect the performance of the catalyst.

In summary, the Fe-zeolites studied are promising catalysts for the oxidative degradation of MTBE in water using H_2O_2. In contrast to homogeneous catalysis by dissolved iron ions (classical Fenton reaction), these heterogeneous catalysts work at neutral pH and can be applied in a fixed-bed reactor whereby the iron is immobilized.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2008.12.014.

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